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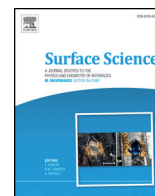
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# Understanding domain symmetry in vanadium oxide phthalocyanine monolayers on Au (111)

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## ABSTRACT

Understanding the growth of organic semiconductors on solid surfaces is of key importance for the field of organic electronics. Non planar phthalocyanines have shown great promise in organic photovoltaic (OPV) applications, but little of the fundamental surface characterization to understand their structure and properties has been performed. Acquiring a deeper understanding of the molecule/substrate interaction in small molecule systems is a vital step in controlling structure/property relationships. Here we characterize the vanadium oxide phthalocyanine (VOPc)/Au (111) surface using a combination of low energy electron diffraction (LEED) and scanning tunneling microscopy (STM), obtaining complex diffraction patterns which can be understood using two dimensional fast Fourier transform (2D-FFT) analysis of STM images. These measurements reveal coexistence of three symmetrically equivalent in-plane orientations with respect to the substrate, each of which is imaged simultaneously within a single area. Combining scanning probe and diffraction measurements allows symmetrically related domains to be visualized and structurally analyzed, providing fundamental information useful for the structural engineering of non-planar phthalocyanine interfaces.

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## 1. Introduction

Creating thin film architectures from small molecule organic semiconductors (SM-OSCs) is the most essential aspect of fabricating organic electronic devices [1]. Within the last decade great progress in the production and optimization of devices (organic photovoltaics (OPVs) [2], organic light emitting diodes (OLEDs) [3] and organic thin film transistors (OTFTs) [4]) has been made. However, many fundamental processes responsible for the formation and properties of the crucial first few layers of active material are not fully understood.

Metallo-phthalocyanine (MPc) molecules are particularly widely used SM-OSCs, due to their ease of synthesis, compatibility with vacuum processing and chemical stability [5]. Planar MPcs such as copper phthalocyanine (CuPc) and iron phthalocyanine (FePc) have been the subject of rigorous surface [6,7], electronic [8,9] and crystal structure [10–12] characterization experiments. Recently non-planar phthalocyanines, in which ionic or covalently bound species are present along with the metal center, have shown a particular promise. Two of the most widely used are aluminium chloride phthalocyanine (ClAlPc) [13,14] and vanadium oxide phthalocyanine (VOPc) [15], but far less fundamental characterization in thin films has been undertaken compared with their planar counterparts.

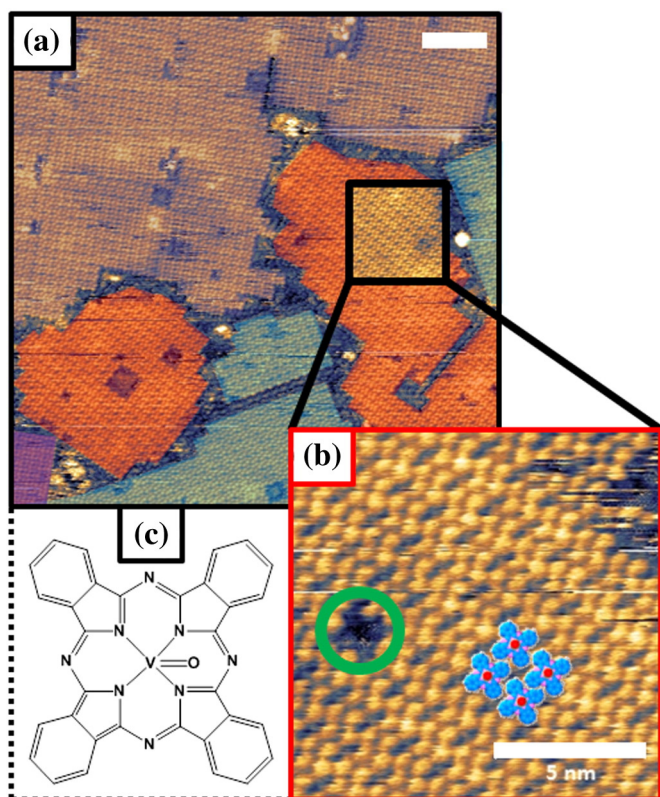
To probe the surface structure of the first monolayer of the non-planar VOPc (vanadium oxide phthalocyanine, Fig. 1(c)) real space surface imaging by scanning tunneling microscopy (STM) has been combined and directly compared with reciprocal space low energy electron diffraction (LEED) on the Au (111) surface. This reveals three unique orientations of VOPc within the first monolayer and provides a deeper understanding of the growth of non-planar MPcs regularly employed in organic electronic devices.

A large scale (75 × 75 nm) STM topography image of the VOPc/Au (111) surface at a coverage of approximately 1 ML is shown in Fig. 1. The inset shows a high resolution image (15 × 15 nm) of the area indicated, with sub-molecular resolution obtained in both. Molecular schematics based on the single crystal structure [16] are overlaid to highlight the packing arrangement, and the green circle highlights a molecular vacancy in the lattice.

The visualization of the local density of states (LDOS) of the molecule is the same as that seen by Hipps et al. [17] and as such we conclude that molecules are lying flat with the Pc ligand  $\pi$  system in the plane of the surface and the oxo-vanadium component projected out into vacuum. This assignment also agrees with the recent photoelectron diffraction experiments of VOPc on the Au (111) surface [18]. The herringbone reconstruction of the underlying gold is also visible in high resolution images (see Supporting Information, Fig. S1) suggesting that it is not lifted or modified by the adsorption of VOPc [17,19]. STM indicates a unit cell of the same dimensions previously observed in the literature, a square unit cell defined by the metal center of the VOPc molecule with

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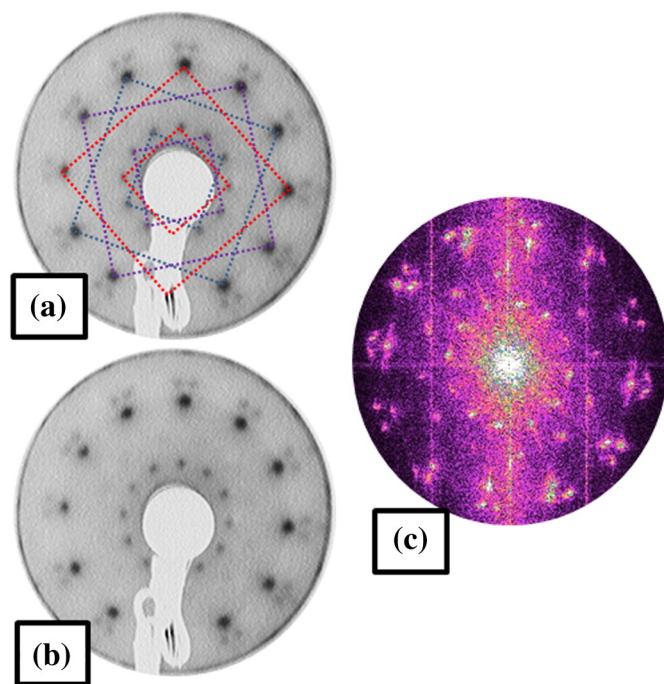


**Fig. 1.** STM images of a VOPc/Au (111) surface at a coverage of approximately 1 ML, (a) large scale ( $75 \times 75$  nm) STM image ( $V_s = -1$  V,  $I = 100$  pA, scale bar is 10 nm), the image has been falsely colored to highlight each rotational orientation (see text) (b) high resolution scan of the area highlighted in (a) with a molecular vacancy highlighted in green and an overlaid packing schematic ( $V_s = -1$  V,  $I = 100$  pA, scale bar is 5 nm) and (c) molecular structure of VOPc. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dimensions of 1.42 nm [17]. Closer inspection of each of the molecular islands reveals three unique rotations of the unit cell across the image, and each of these rotations has been individually colored with an overlay. The energetically equivalent mirror-symmetry domains observed in previous STM images of VOPc/Au (111) [17] were also observed here. The dark purple-shaded (bottom left) portion of Fig. 1(a) shows a region of mirror-symmetry with respect to the rest of the imaged area, and the region shown in the lowest image in Fig. 3 is mirror-symmetric to the other two areas shown therein. Another surface region shown in Fig. S1 (supporting information) displays two adjacent mirror-symmetry domains which have their rotational direction marked by white boxes.

A LEED pattern of the same surface is shown in Fig. 2, demonstrating two concentric rings of twelve spots with even radial spacing and intensity along with a weak outermost ring. This pattern was collected with beam energy of 12 eV due to the large lattice spacings of MPC molecules. No surface degradation was observed by LEED or STM after long (1–2 h) exposure times. The form of the pattern is similar to patterns from films of planar MPCs on the Ag (111) surface [20,21] which confirms that the Pc ligand is lying flat on the surface as is the case with planar MPCs. In the case of iron phthalocyanine on Ag (111) [20] the authors observe a very similar pattern to the one presented here although the (1,1) order spots are present at a low intensity. Other works present in the literature show evidence for charge transfer in phthalocyanines on Ag (111) [22] surfaces and modification of the electronic structure of the interface may be responsible for the presence of the (1,1) spots that are absent in our patterns.

The LEED pattern can be indexed as three identically sized unit cells rotated by  $120^\circ$  with respect to each other about the specular beam (the



**Fig. 2.** LEED pattern of the VOPc/Au (111) interface with (a) and without (b) domains marked at approximately 1 ML (beam energy 12 eV) and (c) 2D-FFT of image (a) shown in Fig. 1.

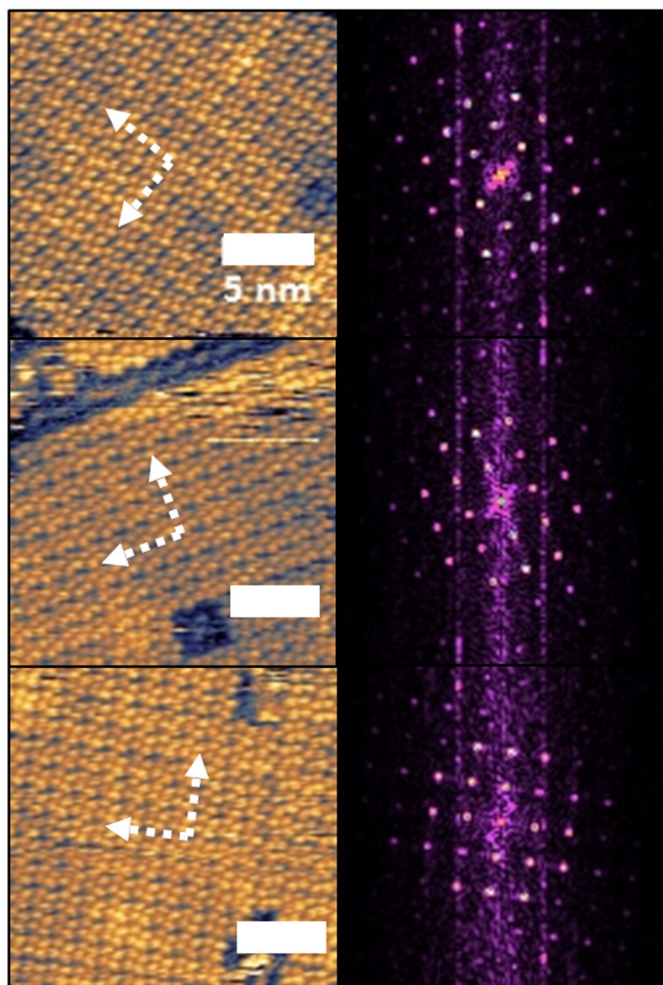
four-fold symmetry of the phthalocyanine lattice makes this appear to be a  $30^\circ$  rotation). Similar patterns were observed and similar structural conclusions were made previously with the related molecule InClPc on the hexagonal (0001) surface of  $\text{MoS}_2$  [23]. Each of the spots within each Laue zone showed similar intensity on the CCD captured images when color-intensity profiles were taken. This suggests that each of the three orientations has comparable population on the surface. It also shows that the features responsible for diffraction are not altered in any of the three orientations.

The large scale STM image in Fig. 1 shows that multiple domains (colored separately) are present and are rotated by around  $120^\circ$  with respect to each other. As an approximation of the reciprocal space structure a 2D-FFT was taken of the real space image and is shown in Fig. 2. When arbitrarily scaled to match the specular beam/pattern distance, it reproduces each of the features observed in the LEED pattern. The only discrepancy between the two is the extra ring of spots between the inner and outer rings. Inspection of LEED patterns of other PCs on (111) surfaces present in the literature (for example, references [21] and [24]) indicate that this missing ring of spots are typically of low intensity, so we assume the same is true in the VOPc system. In order to separate the contribution of each uniquely oriented domain to the overall 2D-FFT sections can therefore be taken from each and independently Fourier transformed (Fig. 3).

Each domain section produces spot patterns with square symmetry with the same dimensions, rotated with respect to each other (about the center of the pattern) by  $30^\circ$ . This suggests domains are symmetrically equivalent with respect to the substrate and the LEED pattern reflects each rotational orientation. The form of the pattern can therefore be understood by considering the alignment of the unit cell in each domain with one of the three principle axes/close packed directions of the Au (111) surface.

The absolute orientation of the VOPc unit cell in each case is not obvious from STM images as concurrent observation of the substrate and overlayer orientation was not possible. LEED patterns of the clean substrate and VOPc layer could not be collected at the same beam energy, which makes relative orientation determination from LEED problematic. By comparing patterns at different energies (see



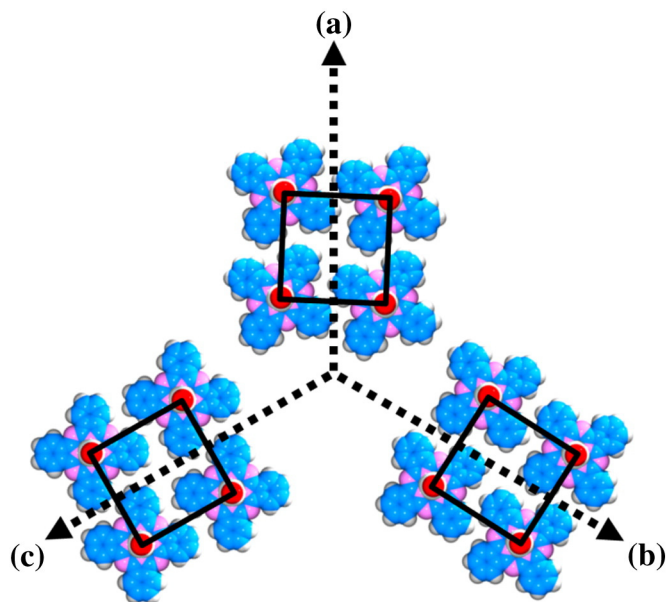


**Fig. 3.** Sections of the STM image in Fig. 1(a) showing different orientations and their corresponding 2D-FFT images. White split arrows highlight the relative orientation of the VOPc unit cell.

Supporting Information, Fig. S2) it is clear that half of the spots (and therefore one of the two unit vectors) of each overlayer unit cell aligns with one of the principle directions of the substrate. Previous studies have suggested small angular rotations of between  $2^\circ$  and  $5^\circ$  of MPc unit cells with respect to Au (111) and Ag (111) surfaces. Pattern distortion and aberration, especially when patterns are collected at vastly different beam energies (12 eV for VOPc, 60–120 eV for Au (111)), make orientation assignment from LEED problematic in this case.

The exact match between the LEED pattern and superposition of the 2D-FFT from each domain indicates that each of the three orientations present on the surface is one of the symmetrically related possibilities. While the rotation of the unit cell relative to the nearest close packed direction remains ambiguous, it must be the same in each case i.e. the angle between the cell axis and the substrate axis is the same. This situation is schematically demonstrated in Fig. 4 with an arbitrary  $4^\circ$  axis offset as observed by England et al. for InClPc on MoS<sub>2</sub> (0001) [23].

In conclusion, large scale sub-molecular resolution real space imaging has been combined with reciprocal space crystal structure determination and comparison between the two has been made using two dimensional fast Fourier transform. Three symmetrically unique orientations of the VOPc monolayer with respect to the Au (111) surface have been identified by STM. The individual contribution of each orientation to the complex LEED pattern has been confirmed. This gives further insight into the growth of the first few layers of a non-planar MPc to be attained without simulation or computational



**Fig. 4.** Schematic of the relative orientation of the VOPc unit cell with each of the principle directions of the Au (111) surface (labeled a, b and c).

treatment. By achieving sufficiently resolved large scale STM images and taking 2D-FFT images directly even complicated LEED patterns can be reproduced and understood. This work provides further understanding of the manner in which these SM-OSCs form the first monolayer, which can be exploited to control properties essential in electronic devices.

## 2. Experimental section

All experiments were conducted at ambient temperature in a custom-built multi chamber UHV system with a base pressure  $< 3 \times 10^{-10}$  mbar. STM images were recorded with an STM/AFM (Omicron®) operated in constant current mode using electrochemically etched polycrystalline tungsten tips. Tips were ultrasonically cleaned in nitric acid, then Ar<sup>+</sup> sputtered and annealed after being loaded in to vacuum. Images were plane corrected and flattened using the open source image processing software Gwyddion, with no further filtering. Two-dimensional fast Fourier transform (2D-FFT) images were also produced using this software. LEED patterns were collected with a SPECTALEED (Omicron®) rear-view MCP-LEED with nano-amp primary beam current. Images of these patterns were captured using a digital CCD camera interfaced to a personal computer. A single crystal Au (111) substrate was used (Surface Preparation Lab (NL), cutting accuracy  $0.1^\circ$ ) and prepared in vacuum by repeated argon sputtering and annealing cycles (Ar<sup>+</sup> energy 1.5 kV annealing temperature  $550^\circ\text{C}$ ). VOPc powder (85% Pure by dye content, Sigma Aldrich, UK) was triply purified by thermal gradient sublimation before use and degassed  $20^\circ\text{C}$  below evaporation temperature ( $T_{\text{evap}} = 265^\circ\text{C}$ ) for several days before use. Standard low-temperature Knudsen effusion cells (Karl Eberl) were used to evaporate the material at a rate of approximately  $0.03 \text{ \AA s}^{-1}$ . Thickness was monitored using calibrated quartz crystal microbalances (QCMs) and checked with STM and ex-situ atomic force microscopy (AFM) measurements using an MFP-3D (Asylum Research, Santa Barbara) operated in tapping mode.

## Notes

The authors declare no competing financial interests.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.susc.2014.05.010>.

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